A STUDY OF SEVERAL NITROGENOUS COMPOUNDS AS FERTILIZER MATERIALS

by

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INTRODUCTION AND REVIEW OF LITERATURE

It is known that nitrogenous fertilizers are required in the high rainfall areas of Kansas. This study was concerned with six liquid and three dry nitrogenous fertilizers and effects of such on wheat and millet plants under greenhouse conditions. The fertilizers used were:

1. $NaSCN-NH_3$
2. $NH_4SCN-NH_3$
3. $NaI-NH_3$
4. NH_4I-NH_3
5. $NH_4NO_3-NH_3$
6. NH_4Br-NH_3
7. NH_4NO_3
8. Urea
9. Ureaform

Considerable work has been accomplished relative to the use of sodium and ammonium thiocyanates as herbicides. Some consideration of these as fertilizer compounds has been made. Thiocyanates mentioned in scientific literature reviewed differed from those used in this experiment in as much as no NH_3 was involved as the solvent.

In 1932 Newton and Paul (16) applied ammonium thiocyanate to a series of wheat plots and to a series of fallow plots. It reduced wheat yields more that year than did sodium dichromate in a similar experiment. It retarded nitrification and did not decompose and lose its toxicity completely during

the season of application, but even in the cases of application of 650 and 1300 pounds per acre the toxic effect disappeared early in the following season. The total and straw yields of crops harvested from these plots the next season generally were increased where either 160 or 325 pounds per acre had been applied and grain yields generally were reduced from 650 and 1300 pounds per acre applications. It also was observed that growth of certain annual weeds was stimulated considerably in 1933 and 1934 by this nitrogenous weed killer in plots which had heavier applications. Laboratory experiments showed that the thiocyanate may be leached out of a soil with water and that it decomposed fairly rapidly in soils under favorable conditions of moisture and temperature but more rapidly in fertile soil rich in organic matter than in poorer soil.

Grigsby (12) applied 10 pounds of NH_4SCN and 80 gallons of water per acre on crabgrass. This treatment left 49 crabgrass seed heads per square foot as compared to 124.25 heads on the untreated check. The chemical had no effect on the other grasses present. When 20 pounds per acre of the chemical were applied there were 6.75 heads per square foot but still no effect on other grasses.

Harvey (13) found that when NH_4SCN was applied to the soil at the rate of 1600 pounds per acre the soil remained sterile for at least four months. When applied at 800 pounds per acre the sterility was less than 120 days.

Sterility lasted from two to four weeks when applied at 320 pounds per acre and stimulation of vegetation occurred after sterility.

Bissey and Butler (1) observed that when NH_4SCN was applied at the rate of 800 pounds per acre there was marked stimulation of growth after 69 days. There was no period of sterility when applied at 100 pounds per acre. Experiments showed that NH_4SCN was more toxic to higher plants than sodium chlorate when compared pound for pound.

DeFrance, et al., (7) mixed white clover, redtop and weed seed together, planted it in the upper three inches of a weedy field soil a few days before treatments of NH_4SCN were applied. When the chemical was applied at three pounds per 1,000 square feet the growth of nearly all of the weeds was inhibited. A lapse of four weeks after treatment was required for satisfactory ryegrass growth and six weeks lapse of time was required for redtop to grow.

DeFrance and Simmons (8) applied NH_4SCN at the rate of two pounds per 1,000 square feet with good control of weeds. Crops seeded four weeks after treatment grew satisfactorily.

Carlson and Moulton (4) applied NH_4SCN to the soil where quackgrass three to ten inches in height was growing. The killing effect was more pronounced when applied to young plants as compared with applications to taller and better established quackgrass.

Sandhoff and Skinner (17) reported that seven months

after NH_4SCN had been applied to soil there was little if any available nitrogen in the soil above that which could be accounted for as coming from the NH_4^+ radical and soil organic nitrogen.

These workers also reported that addition of 1.25 per cent ammonium thiocyanate to unlimed garden soil caused neither increase nor decrease in algae or protozoa. With the same concentration of either NaSCN or NH_4SCN the number of bacteria definitely decreased after three and five weeks. With 0.125 per cent NH_4SCN there was no pronounced change in bacterial numbers in seven weeks, but in nine weeks there was definite reduction.

Additions of 0.075 per cent ammonium or sodium thiocyanate to limed soil always caused a significant increase in bacterial numbers over the control when determinations were made at two week intervals for periods up to 28 weeks. When one per cent NaSCN was added to unlimed garden soil little of the theoretical thiocyanate nitrogen could be recovered as ammonia or nitrate at any time up to seven weeks incubation. When one per cent ammonium thiocyanate was added to unlimed garden soil less than 100 per cent of the theoretical ammonical nitrogen could be accounted for after two or more weeks incubation. Addition of 0.075 per cent ammonium thiocyanate to limed soil resulted in an average recovery of 49.7 per cent of the theoretical nitrogen (99.45 per cent of the ammonium nitrogen) in biweekly determinations

made over a period of 28 weeks. It also was shown that when 0.075 per cent sodium thiocyanate was added to limed soil an average of 37.1 per cent of the theoretical thiocyanate radical was recovered as ammonia or nitrates in the biweekly determinations made for as long as 28 weeks.

Smith, et al., (18) reported ammonium thiocyanate was inhibitive and bactericidal to bacteria and actinomyces but stimulatory to fungi. Depressive effect on total counts and actinomyces did not appear until after ten days, whereas beneficial effect on fungi was apparent in three days. Ammonium thiocyanate had very little, if any, effect upon soil protozoa.

Hurd-Karrer (14) added five grams of NH_4SCN and 5.3 grams of NaSCN separately to three lots of soil. One lot of soil had pH of 5.1, one lot had pH of 6.8 and the other had pH of 7.7. Barley and oats were sown two days later in alternating rows in each of the soils. Both thiocyanates killed all the plants of the first crop soon after emergence but when resown six weeks later lethal effects were apparent in unlimed plots only. In plots having pH values of 6.8 and 7.7 both had decomposed to such an extent that there was no sign of toxicity and the growth was so stimulated that green weights were about 25 per cent higher than those of control plants.

This worker reported that there was no sign of toxicity in any of the plots when planted the third time (three months

after the applications). Acid soil which had lethal properties at time of the second sowing now produced plants averaging from 47 to 89 per cent larger than corresponding controls. It was concluded that stimulation which so consistently followed injury by NH_4SCN application could not be attributed to ammonium nitrogen since similar degrees of stimulation were obtained with the application of sodium salt.

Thomas, et al., (20) used NH_4SCN as a defoliant treatment on cotton at the rate of 10.5 pounds per acre. Eighty per cent defoliation resulted from application of thiocyanate as compared to 36.3 per cent with no treatment.

Steinbauer and Steinmetz (19) used NH_4SCN to kill trees. Wild plum trees with stem diameters varying from a few inches to a foot or more were treated either by pouring NH_4SCN solution into the wood where it had been frilled by an axe or by pouring the solution into $\frac{3}{4}$ inch holes drilled into the trees about three inches deep. The holes were slanted downward and were about three inches apart around the circumference of the tree. Two pounds of the chemical in one gallon of water proved toxic and killed the entire trees including sprouts. It was reported that pouring solution into the hole was more effective than pouring it into the wood frilled with an axe.

The most logical use of NH_4SCN in weed control, according to Crafts (6) is against annuals and shallow-rooted perennials

in pastures or turf lands where the crop plants may rapidly occupy the areas made bare upon death of weeds. By utilizing the nutrients that result upon decomposition of the herbicide, the crop should thrive and present greater competition to any seedlings that might grow from seed germinating in the soil. This worker concluded that since sodium tends to replace calcium in the replaceable base complex of soils, with a corresponding deflocculation of the colloids and decrease of permeability to water, sodium thiocyanate could not be recommended for repeated use on western soil.

King (15) took corn leaves of seedlings that were 15 to 25 days old and immersed the terminal nine centimeters in a one per cent concentration of NaSCN and an identical concentration of NH_4SCN. The distance of injury from NH_4SCN treatment was 18 centimeters in 24 hours, 21 centimeters in 48 hours and the entire plant in seven days. The same was true for the NaSCN except there was no injury at the 24 hour period.

An experiment involving soaking of potatoes in one per cent solution of NaSCN was performed by Buchanan (3). The potatoes previously had been cut in pieces for planting and then soaked in NaSCN solution. After soaking for one hour the pieces then were planted without rinsing. Pieces which had been allowed to soak in NaSCN produced sprouts more rapidly than those which had been soaked in water for the same length of time.

Lethal concentration of ammonium thiocyanate with duckweed was found by Fromm (10) to be 10^{-3} M.

Gleen (11) claimed thiocyanate at a high concentration of .01 M, when perfused through an enriched nitrifying soil, had only a partially inhibitive influence on the oxidation of ammonium sulphate. It further inhibited the oxidation of ammonium nitrogen to nitrite nitrogen by 24 per cent and nitrite nitrogen to nitrate nitrogen by 62 per cent. After thiocyanate had been perfused through a partially enriched nitrifying soil for four or five days it was metabolized to ammonium sulphate by specific thiocyanate oxidizing microorganisms which thrive in the soil. Soil then might be enriched by three specific groups of soil microflauna and two groups of oxidizing bacteria which serve as nitrifiers. Gleen also stated that by using enriched nitrifying soils ammonium cations were oxidized rapidly to nitrate with very little nitrite formation. When thiocyanate was perfused through a similar soil it was not metabolized until after a lag, suggesting that growth of its specific oxidizing microorganisms took place and build up of nitrite occurred because of oxidation by the nitrifying organisms already present in the soil of the ammonium cations formed.

Conrad (5) found that NaSCN was toxic to the first crop of milo planted but lost its toxicity when the second crop was planted about 45 days later. Not only had it lost its toxicity but at least some of the sulfur had become available.

About 1873 Divers (9) prepared liquid NH_4NO_3-NH_3 by bringing dry ammonia gas into contact with dry ammonium nitrate in a flask embedded in ice and loosely closed by a stopper. The tube conveying the ammonia passed through the stopper and nearly reached the bottom of the flask. The nitrate was dried by spreading the crystals on the floor of an air tight glass chamber for a month or more with dishes of sulfuric acid inside or by placing in an oven for several hours at a temperature just a little below its melting point. The ammonia was dried by passing through a long coiled tube surrounded with ice and then passing through a glass tube of more than 50 centimeters in length which was packed with very small pieces of stick potash. The nitrate soon started to deliquesce in ammonia and after awhile entirely liquified.

Divers reported that at 0°C and one atmosphere of pressure ammonium nitrate condensed almost exactly half its weight of ammonia. The NH_4NO_3-NH_3 produced by this method often is referred to as "Divers' solution".

Experiments by Bradley and Alexander (2) showed that at room temperature ammonium thiocyanate absorbed 44.78 per cent and 45.26 per cent of its own weight of ammonia in two separate trials. At 0°C the product had 43.10 per cent ammonia, at 25°C had 31.16 per cent NH_3, at 50°C had 19.40 per cent, at 75°C had 6.17 per cent, and 0 at 100°C.

METHODS OF STUDY

Soil Material Used

Sandy soil from the surface six inches was obtained in February 1956 from the Ashland Agronomy Farm near Manhattan, Kansas. This alluvial soil is found adjacent to the Kansas River.

Fertilizers Used

Ammonium nitrate and urea used in this experiment were ordinary fertilizer materials which are familar to the fertilizer industry. These were used in this experiment for comparison purposes. The other types were not so common.

Ureaform is a material of low availability of nitrogen. It is a combination of urea and formaldehyde. Its practical use is to furnish nitrogen throughout the growing season by not allowing all to become available soon after application.

The NH_4NO_3-NH_3, NH_4SCN-NH_3, NH_4Br-NH_3, NH_4I-NH_3 are liquid types and are quite corrosive fertilizer substances. The NaI-NH_3 and NaSCN-NH_3 compounds were also liquids. The NH_4I-NH_3, NH_4NO_3-NH_3 and NH_4Br-NH_3 had to be kept at a low temperature when applying unless applied under pressure. This was required because of the low boiling point of each of these materials.

Some of the chemical properties of the liquid fertilizers are enumerated in Table 1.

Table 1. Properties of chemicals used as fertilizers.

Fertilizer material	Condensation temperature	Freezing point	Moles of NH_3 per mole of chemical used	Boiling point
NaI-NH_3	24°C	3°C	3.6	42°C
NH_4I-NH_3	0°C	<0°C	2.6	25°C
NaSCN-NH_3	Room Temp.	<0°C	2.7	34°C
NH_4SCN-NH_3	Room Temp.	<0°C	1.4	64°C
NH_4Br-NH_3	0°C	<0°C	2.5	4°C
NH_4NO_3-NH_3	0°C	<0°C	1.6	20°C

Greenhouse Procedure

Soil was brought into the greenhouse, spread out on a table and thoroughly mixed. Two thousand grams of the soil were placed in each of 170 pots. Fifteen spring wheat seeds of Pusa 52 X Federation and an equivalent rate of 500 pounds of triple super phosphate were placed in each pot on March 3, 1956.

The nitrogenous fertilizers were applied after the wheat had started to emerge. Fertilizers were applied at rates of 100, 200, and 300 pounds of nitrogen per acre and this amount was applied to each of six containers so that 18 pots were required for each fertilizer (six for 100 pound rate, six for 200 pound rate, and six for the 300 pound rate). Eight pots were used for untreated controls. Liquid fertilizers were applied with a small tuberculin syringe while weighed amounts of the dry fertilizer were applied by hand.

The amount of fertilizer applied to each individual container is shown in Table 2.

All wheat cultures that survived were allowed to mature and then harvested, dried, weighed and nitrogen content determined.

After the wheat was harvested all of the pots were replanted to millet but no additional fertilizer was added. These plants were allowed to grow to maturity and then harvested, dried, weighed and nitrogen content determined.

Table 2. Rates of fertilizer application.

Fertilizer	Number of pots at each application rate	Rate of application of nitrogen pounds per acre	Amount of fertilizer applied to each pot
NH_4NO_3	6	100	0.3 grams
"	6	200	0.6 grams
"	6	300	0.9 grams
Urea	6	100	0.22 grams
"	6	200	0.44 grams
"	6	300	0.66 grams
Ureaform	6	100	0.27 grams
"	6	200	0.54 grams
"	6	300	0.81 grams
NH_4NO_3-NH_3	6	100	0.225 ml.
"	6	200	0.45 ml.
"	6	300	0.675 ml.

Table 2. (concl.)

Fertilizer:	Number of pots at each application rate:	Rate of application of nitrogen pounds per acre	Amount of fertilizer applied to each pot
$NH_4SCN-NH_3$	6	100	0.267 ml.
"	6	200	0.534 ml.
"	6	300	0.801 ml.
$NaSCN-NH_3$	6	100	0.213 ml.
"	6	200	0.426 ml.
"	6	300	0.639 ml.
NH_4Br-NH_3	6	100	0.24 ml.
"	6	200	0.48 ml.
"	6	300	0.72 ml.
NH_4I-NH_3	6	100	0.283 ml.
"	6	200	0.566 ml.
"	6	300	0.849 ml.
$NaI-NH_3$	6	100	0.398 ml.
"	6	200	0.796 ml.
"	6	300	1.194 ml.
No Treatment	8	000	0.000

Laboratory Analyses

After harvesting, the plants were dried, threshed, and weighed. Each material from each pot was weighed separately. Straw and the grain were not separated in the millet crop but were weighed together. After recording of weights plant

materials were ground in an electric grinder in preparation for nitrogen determinations.

Nitrogen content was determined by the Kjeldahl method. This consisted of weighing a known amount of sample (usually one gram) which was then placed in a Kjeldahl flask. A digestion mixture of K_2SO_4, $FeSO_4$ and $CuSO_4$ and 30 ml. of H_2SO_4 was added to the sample and then placed on the digestion rack until digestion was complete. After allowing to cool for 4-5 hours, water was added to the sample and cooling was allowed to occur. One-hundred milliliters of 12 N sodium hydroxide was added plus three or four pieces of zinc. The flask was placed on the distillation rack. The distillate was collected in 50 milliliters of boric acid and back titrated with H_2SO_4 of known normality. The nitrogen content of the materials was calculated.

Method of Preparing Liquid Fertilizers

All of the liquid fertilizers used in the experiment were prepared under the supervision of Dr. C. W. Leonard of the Kansas State College Chemistry Department. A weighed amount of each chemical (NaSCN, NH_4SCN, NH_4NO_3, NH_4Br, NaI, NH_4I) was placed in a suitable container such as a two liter bottle. The container was kept in a constant temperature bath maintained at 0°Centigrade by melting ice. Anhydrous ammonia was passed through the salt until the system reached a vapor pressure equilibrium with one atmosphere pressure at

0°Centigrade. The resulting solutions then contained from 1.4 to 3.6 moles of ammonia per mole of chemical used.

EXPERIMENTAL RESULTS

Crop Growth

All wheat plants were green and growing when fertilizers were applied. Wilting began to occur in cultures treated with thiocyanate fertilizers three days after application and continued until death resulted. Wilting became evident in the iodide fertilizers 11 days after application and eventually death occurred. Bromide fertilizer caused plants to wilt one day after application but death did not occur. Following this, partial recovery and some growth occurred.

Containers which had received thiocyanate fertilizer and in which plants died were replanted with wheat one month after the fertilizer application. Plants emerged and did not start to wilt until two weeks after planting or 10 days after emergence and continued to wilt until dead.

Iodide cultures were replanted to wheat six weeks after fertilizer application. Plants emerged and grew satisfactorily at first but started wilting two weeks after planting and did so until dead.

Iodide and thiocyanates again were replanted with wheat 80 days after the original fertilizer application. Again wilting started two weeks after planting and continued in

the iodide treatments until death occurred but this was not necessarily true in the thiocyanate cultures. Some of the containers with the three rates of thiocyanate application had no plants alive while some had erratic results in that two or three plants lived but did not grow satisfactorily.

The NH_4NO_3, ureaform, urea, NH_4NO_3-NH_3 and untreated cultures all grew satisfactorily during the lethal period of thiocyanate and iodide. The NH_4NO_3-NH_3 crop had a dark green color and looked exceptionally well when compared to the checks. Ureaform treatments did not produce as much growth as urea, NH_4NO_3 and NH_4NO_3-NH_3 and had some yellowing in some of the plants. These crops were harvested upon maturity which occurred 93 days after planting.

All containers with the various fertilizers and different rates of applied nitrogen were replanted to millet 145 days after application of the fertilizer but no additional fertilizer was applied. All pots had satisfactory growth at first but again iodide treatments caused wilting and eventual death of plants. All other applications grew satisfactorily, especially the NaSCN-NH_3 and NH_4SCN-NH_3. The thiocyanate treatments had much darker green color than any other fertilizer application and produced more growth. The dark green color evident with NH_4NO_3-NH_3 in the case of the wheat crop was not evident with the millet crop. The bromide treated cultures stayed green longer than any of the others but all pots were harvested 62 days after planting.

Wheat Crop

Average Yield of Straw. Average straw yield of cultures which survived was increased over the control by all treatments except that of NH_4Br-NH_3. Decrease in average straw yield of the NH_4Br-NH_3 treatment was great enough to be statistically significant when compared to no treatment. The yield was more than doubled when compared to no treatment by all rates of application of NH_4NO_3-NH_3. This was true for 200 and 300 pound rates of nitrogen application of ammonium nitrate and for the 200 pound rate of nitrogen application in the form of urea. Significant increases in the average yield of straw occurred, as shown in Appendix Table 3, for all treatments except NH_4Br-NH_3 and the 100 and 200 pound rate of nitrogen in ureaform when compared with no treatment.

Average Yield of Grain. As seen in Table 3, the average yield of wheat grain from the pots with the various fertilizer treatments was higher than no treatment yield in all cases except for use of NH_4Br-NH_3. Ureaform treatment again produced lower average yield than the other fertilizers. Significant increases in average grain yield occurred for all treatments except where 100 pounds of nitrogen were furnished by ureaform and where all of the NH_4Br-NH_3 treatments were involved.

Yield of grain in the NH_4NO_3-NH_3 containers was highest at the 100 pound rate of nitrogen application and was significantly higher at this rate of nitrogen application when

compared to either the 200 or 300 pound rate. In this experiment additional applied nitrogen was harmful rather than beneficial insofar as increasing grain yield was concerned. The higher rates were significantly superior to no treatment, however. The NH_4NO_3 treatments acted similarly in that the highest grain yield occurred for application of 100 pounds per acre of nitrogen.

Average Per Cent Nitrogen in Grain. The average per cent of nitrogen in wheat grain produced from all ureaform cultures and from the 100 pound rates of nitrogen supplied by either NH_4NO_3 or urea were about the same as that produced by no treatment. All other applications produced significantly higher percentages of nitrogen when compared to no treatment. The higher percentages were produced by NH_4Br-NH_3 and NH_4NO_3-NH_3 as indicated in Table 3. The increases in percentage of nitrogen of grain produced by use of NH_4Br-NH_3 and NH_4NO_3-NH_3 were significant when compared to the same rates of application of urea and NH_4NO_3.

Average Per Cent Nitrogen in Straw. The average per cent nitrogen in wheat straw followed almost the same trend as did the average per cent nitrogen in grain. Again the low percentages were produced by ureaform applications, the 100 pound rate of nitrogen furnished by NH_4NO_3, or urea and no treatment. Percentages of nitrogen in straw were significantly higher when compared to no treatment for all rates of application of NH_4Br-NH_3, the 300 pound rates of nitrogen supplied

either by urea or NH_4NO_3 and the 200 and 300 pound rates of nitrogen furnished by NH_4NO_3-NH_3. The content was six times as great for the 300 pound rate of nitrogen in the form of NH_4Br-NH_3 as compared to no treatment.

The NH_4NO_3-NH_3 and NH_4Br-NH_3 treatments produced significantly increased nitrogen percentages for the 200 and 300 pound rates of nitrogen application when compared with the same rates of application of NH_4NO_3 and urea. The highest percentage was found in the 200 and 300 pound application of nitrogen in the liquid NH_4Br-NH_3. These data also are presented in Appendix Table 3.

Average Total Nitrogen Content in Crop. The average total nitrogen contents of the wheat crop increased as the rate of application of the various fertilizers increased. The NH_4NO_3-NH_3 fertilizer produced a three-fold increase in total nitrogen content when compared to no treatment. The 100 pound per acre nitrogen application of NH_4NO_3-NH_3 caused as much accumulation of nitrogen by plants as did the use of 200 pounds per acre of nitrogen of either NH_4NO_3 or urea. Significant increases occurred for all treatments except the 100 and 200 pound rates of nitrogen supplied by ureaform. It was noted that even though the yield of grain and straw was low for NH_4Br-NH_3 treatments average total nitrogen contained in the wheat crop still was significantly higher than for no treatment because of its high percentage of nitrogen. This information is presented graphically in Fig. 7.

Millet Crop

Millet was the second crop grown to maturity in all pots except those which received NH_4SCN-NH_3 and NaSCN-NH_3 treatments. The millet crop was the first to survive in the thiocyanate treatments because of the earlier lethal effects of the fertilizer.

Average Yield. Significant increases in the average yield of millet occurred for all NaSCN-NH_3 treatments, the 200 and 300 pound rates of nitrogen supplied by NH_4SCN-NH_3 and NH_4NO_3-NH_3, the 300 pound rates of nitrogen of NH_4Br-NH_3 and urea, and the 100 pound nitrogen applications of NH_4NO_3 and ureaform when compared to no treatment. Highest yields were produced by NaSCN-NH_3, NH_4SCN-NH_3 and NH_4NO_3-NH_3 treatments.

These results are presented in Appendix Table 4.

Average Per Cent Nitrogen. The NH_4SCN-NH_3 treatments gave significant increases at all three rates of application when compared to no treatment. The per cent nitrogen in plant material produced by 300 pound rate of nitrogen application of this compound was over three times as great as per cent nitrogen in plants produced by no treatment.

The use of NaSCN-NH_3 gave significant increases for the 200 and 300 pound rates of nitrogen application but the 100 pound rate produced a content similar to no treatment.

The use of either NH_4Br-NH_3 or ureaform at 300 pound

rates of nitrogen application also produced significant increases. There were no significant decreases, as can be seen in Fig. 4 in the Appendix.

The 300 pound rate of nitrogen application of NH_4NO_3-NH_3 produced material with significantly higher nitrogen content than did the same rate of NH_4NO_3.

Average Total Nitrogen in Crop. The 300 pounds per acre of nitrogen in the NH_4SCN-NH_3 fertilizer produced more than five times as much total nitrogen in plants as did no treatment. The 200 pound nitrogen rate of NH_4SCN-NH_3 and the 200 and 300 pound nitrogen rates of $NaSCN$-NH_3 produced between three and four times as much nitrogen in plants as did no treatment. Significant increases also were present for the 300 pound nitrogen rates of NH_4Br-NH_3, NH_4NO_3-NH_3, and urea and the 100 pound rate of nitrogen application of $NaSCN$-NH_3 as shown in Fig. 4.

When applied at 300 pounds of nitrogen per acre NH_4NO_3-NH_3 produced significantly more nitrogen in plants than did either urea or NH_4NO_3 at the same rate of application.

Average Total Nitrogen Uptake in Combined Crops of Wheat and Millet

Every treatment, except where 100 pounds per acre of nitrogen were supplied by either NH_4Br-NH_3, urea or ureaform and where 200 pounds per acre were supplied by ureaform, produced a significant increase in nitrogen uptake. (Appendix Table 5 and Fig. 11). The greatest uptake was produced by

use of 300 pounds per acre of nitrogen in the form of NH_4NO_3-NH_3. This material consistently produced greater total uptake of nitrogen than did any of the other materials at comparable rates of application. In all except two instances it was significantly superior to all other comparable treatments.

The material, NH_4Br-NH_3, despite its inferiority with the wheat crop, apparently yielded more nitrogen which was available to plants than did ureaform. This was especially true at the highest rates of application.

SUMMARY AND CONCLUSIONS

The results of this study of various nitrogenous fertilizers showed desirable characteristics for some but not for all of the liquids.

The total length of the toxic period for NH_4I-NH_3 and NaI-NH_3 was not determined but the plants did not grow when planted about five months after date of initial fertilizer application.

The NH_4NO_3-NH_3 proved very successful in increasing not only the yield of grain and straw but also increasing the per cent of nitrogen in each in the first crop. This greatly increased total uptake of nitrogen. There was no toxic effect for this material. It produced luxuriant dark green growth in the first crop grown. Increased nitrogen uptake still occurred with the second crop where higher rates of

application were involved.

The $NaSCN-NH_3$ and $NH_4SCN-NH_3$ treatments were toxic to wheat plants when first applied but lethal effects disappeared in about five months. This toxic effect undoubtedly was caused by the lethal effects of the thiocyanate. Presumably when this form of nitrogen disappeared as a result of bacterial action the nitrogen originally present in the thiocyanate radical became available for plant utilization. Plants then grew about the same as where $NH_4NO_3-NH_3$ had been applied. High nitrogen uptake by plants occurred for high rates of application of nitrogen. These two fertilizers might have possibilities as a combination herbicide and fertilizer. A two-fold mission of first eradicating weeds and then stimulating plant growth might result from properly timed applications.

The use of NH_4Br-NH_3 increased nitrogen uptake with the first crop but caused lower yields of grain and straw when compared with no treatment. The yield decrease undoubtedly resulted from physiological disturbances associated with wilting induced at time of initial application. Yield of grain and straw still was comparatively low with the second crop for low rates of application. These increased with increased application rates. It appeared that usefulness of this fertilizer compound was less than that of either $NaSCN-NH_3$ or $NH_4SCN-NH_3$ and certainly it was less than that of $NH_4NO_3-NH_3$. This inefficiency was because of its tendency

merely to inhibit growth when first applied without having the ability to serve as an effective herbicide.

Ureaform was no more effective than no treatment in many respects. Low availability of its nitrogen undoubtedly was responsible for this behavior.

Use of either urea or NH_4NO_3 produced consistently greater nitrogen uptake by plants than no treatment. Usually these treatments ranked in between no treatment and NH_4NO_3-NH_3, $NaSCN$-NH_3, and NH_4SCN-NH_3.

Need for additional study with respect to any or all of the liquid fertilizers, especially under field conditions and with different soils, was suggested by these results.

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LITERATURE CITED

(1) Bissey, R. and O. Butler.
Effect of applications of sodium chlorate and ammonium thiocyanate on subsequent sowings of wheat. Jour. Amer. Soc. Agron. 26:838-46. 1934.

(2) Bradley, W. P., and W. B. Alexander.
Action of ammonia upon ammonium thiocyanate. Jour. Amer. Chem. Soc. 34:15-24. 1912.

(3) Buchanan, A. E., Jr.
Chemical alarm clocks arouse sleepy plants. Scientific Amer. 140:116-117. 1929.

(4) Carlson, R. F., and J. E. Moulton.
Use of ammonium salt of trichloroacetate, the sodium salt of trichloroacetate, ammonium thiocyanate, and herbicide "PB", in the eradication of grasses, and the effect of these chemicals on strawberry and raspberry plants. Mich. Agr. Expt. Sta. Quart. Bul. 4. 30:413-21. 1948.

(5) Conrad, J. P.
Retention by soils of the sulfur of various compounds as revealed by subsequent plant growth. Jour. Amer. Soc. Agron. 33:37-46. 1941.

(6) Crafts, A. S.
Toxicity of certain herbicides in soils. Hilgardia. 16:459-83. 1945.

(7) DeFrance, J. A., R. S. Bell and T. K. Odland.
Killing weed seeds in the grass seedbed by the use of fertilizers and chemicals. Jour. Amer. Soc. Agron. 39:530-35. 1947.

(8) DeFrance, J. A., and J. A. Simmons.
Inhibiting weeds in seedbeds with chemicals. Proc. Amer. Soc. Hort. Sci. 57:355-60. 1951.

(9) Divers, E.
On the union of ammonium nitrate with ammonia. Philosophical Transactions of the Royal Soc. of London. 163:359-76. 1873.

(10) Fromm, F.
A quantitative evaluation of the lemna test for herbicides. Botannical Gazette. 113. 1:86-90. 1951.

(11) Gleen, H.
Microbiological oxidation of ammonium and thiocyanate ions in soil. Nature. 168:117-118. 1951.

(12) Grigsby, B. H.
Control of crabgrass by the use of chemical sprays. Mich. Agr. Expt. Sta. Quart. Bul. 32. 479-85. 1950.

(13) Harvey, R. B.
Ammonium thiocyanate as a weed eradicant. Jour. Amer. Soc. Agron. 23:944-46. 1931.

(14) Hurd-Karrer, A. M.
Relation of soil reaction to toxicity and persistence of some herbicides in greenhouse plots. U. S. Dept. of Agr. Tech. Bul. 911. 1946.

(15) King, L. J.
A leaf immersion technique for studying the absorption and translocation of chemicals in plants. Contributions from Boyce Thompson Inst. 15:165-171. 1948.

(16) Newton, J. D. and A. D. Paul.
Decomposition and movement of herbicides in soils, and effects on soil microbiological activity and subsequent crop growth. Part II Can. Jour. Research. 13:101-14. 1935.

(17) Sandhoff, A. G. and C. E. Skinner.
The nitrification of ammonium thiocyanate (a weed eradicant) and the effect of this compound upon the soil population. Soil Sci. 48:287-294. 1939.

(18) Smith, N. R., V. T. Dawson, and M. E. Wenzel.
The effect of certain herbicides on soil microorganisms. Soil Sci. Soc. Amer. 10:197-201. 1945.

(19) Steinbauer, G. P. and F. H. Steinmetz. Eradication of certain Maine weeds, an important step in control of potato diseases spread by aphids. Maine Agr. Expt. Sta. Misc. Pub. 602. 1945.

(20) Thomas, H. O., W. F. Buchele, and J. M. Jackson. Chemical defoliation of cotton. Ark. Agr. Expt. Sta. Rep. Ser. 27. 1951.

APPENDIX

Table 3. Effect of various fertilizer treatments on yield and nitrogen content of wheat.

Fertilizer	Pounds of N per A	Average[1] Yield of grain (gm./pot)	Yield of straw (gm./pot)	Per cent N in grain	Per cent N in straw	Total N in grain (mg./pot)	Total N in straw (mg./pot)	Total N in crop (mg./pot)
NH_4Br-NH_3	100	1.37	2.88	2.70	0.66	36.93	18.44	55.37
NH_4Br-NH_3	200	1.29	2.80	3.03	1.08	38.82	30.07	68.89
NH_4Br-NH_3	300	1.30	2.70	3.24	1.20	41.76	32.30	74.06
NH_4NO_3	100	4.14	5.14	1.45	0.15	61.03	7.92	68.95
NH_4NO_3	200	3.78	7.71	1.84	0.28	69.33	20.52	89.85
NH_4NO_3	300	2.84	7.40	2.21	0.66	62.69	48.22	110.91
Urea	100	3.38	4.69	1.44	0.13	48.70	6.17	54.87
Urea	200	4.24	7.72	1.89	0.23	79.82	17.85	97.67
Urea	300	2.96	6.31	2.33	0.50	68.90	30.97	99.87
Ureaform	100	1.98	4.11	1.51	0.14	30.04	5.82	35.87
Ureaform	200	2.80	3.60	1.51	0.17	42.40	6.15	48.55
Ureaform	300	2.98	4.52	1.59	0.20	47.38	9.15	56.53

Table 3. (concl.)

Fertilizer	Pounds of N per A	Average[1] Yield of grain (gm./pot)	Yield of straw (gm./pot)	Per cent N in grain	Per cent N in straw	Total N in grain (mg./pot)	Total N in straw (mg./pot)	Total N in crop (mg./pot)
NH_4NO_3-NH_3	100	4.10	7.20	2.02	0.24	81.77	16.88	98.65
NH_4NO_3-NH_3	200	2.91	7.14	2.41	0.50	67.49	36.69	104.18
NH_4NO_3-NH_3	300	2.64	7.36	2.87	0.94	75.59	69.51	145.10
No treatment	0	1.84	3.55	1.57	0.20	28.24	7.57	35.81
L. S. D.[2]	(.05)	0.80	0.80	0.22	0.15			15.92
L. S. D.[3]	(.05)	0.74	0.74	0.20	0.14			14.92

[1] Average of six replications for fertilizer treatments and eight replications for no treatment.
[2] For comparison of fertilizer with fertilizer.
[3] For comparison of fertilizer with no treatment.

Table 4. Effect of various fertilizer treatments on yield and nitrogen content of millet.

Fertilizer used	Pounds of N per acre	Average[1]		
		Yield of straw and grain (gms./pot)	Per cent nitrogen in crop	Total nitrogen in crop (mg./pot)
NH_4Br-NH_3	100	1.14	1.00	11.29
NH_4Br-NH_3	200	2.40	0.92	22.24
NH_4Br-NH_3	300	3.05	1.66	48.84
NH_4NO_3	100	3.02	1.06	31.30
NH_4NO_3	200	2.20	1.17	25.01
NH_4NO_3	300	2.71	1.08	29.18
Urea	100	1.87	1.12	20.68
Urea	200	2.58	1.21	30.90
Urea	300	2.90	1.34	37.90
Ureaform	100	2.82	0.92	25.98
Ureaform	200	2.11	1.46	31.11
Ureaform	300	1.99	1.48	30.90

Table 4. (concl.)

Fertilizer used	Pounds of N per acre	Average[1] Yield of straw and grain (gms./pot)	Per cent nitrogen in crop	Total nitrogen in crop (mg./pot)
NH_4NO_3-NH_3	100	2.43	1.03	24.63
NH_4NO_3-NH_3	200	3.28	1.08	35.51
NH_4NO_3-NH_3	300	3.36	1.76	60.59
NaSCN-NH_3	100	3.49	1.28	45.12
NaSCN-NH_3	200	3.75	2.28	85.65
NaSCN-NH_3	300	3.42	2.22	71.20
NH_4SCN-NH_3	100	2.31	1.76	36.20
NH_4SCN-NH_3	200	3.33	2.39	76.59
NH_4SCN-NH_3	300	3.43	3.59	120.41
No treatment	0	2.00	1.10	22.02
L. S. D.[2] (.05)		0.83	0.40	15.64
L. S. D.[3] (.05)		0.79	0.38	14.65

[1] Average of six replications for fertilizer treatments and eight replications for no treatment.
[2] For comparison of fertilizer with fertilizer.
[3] For comparison of fertilizer with no treatment.

Table 5. Total nitrogen uptake in wheat and millet crop combined for various fertilizer treatments.

Fertilizer material	Pounds of nitrogen per acre	Average[1] total nitrogen in crops (mg./pot)
NH_4Br-NH_3	100	66.66
NH_4Br-NH_3	200	91.13
NH_4Br-NH_3	300	122.90
NH_4NO_3	100	100.25
NH_4NO_3	200	114.86
NH_4NO_3	300	140.09
Urea	100	75.55
Urea	200	128.57
Urea	300	137.77
NH_4NO_3-NH_3	100	123.28
NH_4NO_3-NH_3	200	139.69
NH_4NO_3-NH_3	300	205.69
Ureaform	100	61.85
Ureaform	200	79.66
Ureaform	300	87.43
No treatment	0	57.83
L. S. D.[2] (.05)		23.44
L. S. D.[3] (.05)		21.93

[1] Average of six replications for fertilizer treatments and eight replications for no treatment. Includes the nitrogen uptake of wheat and millet combined.
[2] For comparison of fertilizer with fertilizer.
[3] For comparison of fertilizer with no treatment.

EXPLANATION OF PLATE I

Fig. 1 The effect of NH_4SCN-NH_3 on wheat plants seven days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of $NaSCN$-NH_3 on wheat plants seven days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE I

Fig. 1

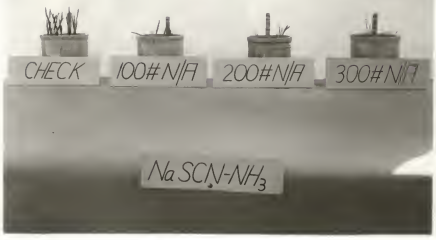


Fig. 2

EXPLANATION OF PLATE II

Fig. 1 The effect of NaI-NH_3 on wheat plants seven days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of NH_4I-NH_3 on wheat plants seven days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE II

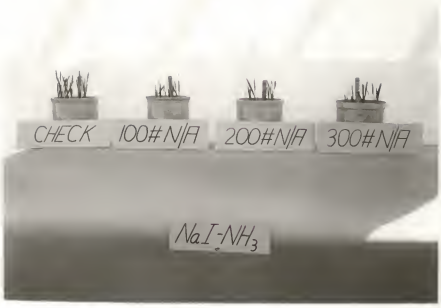


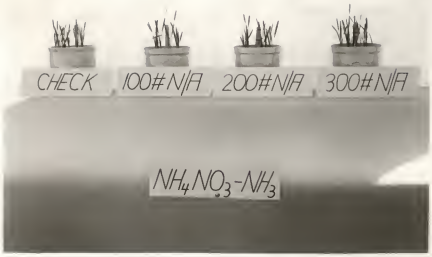
Fig. 1

Fig. 2

EXPLANATION OF PLATE III

The effect of NH_4NO_3-NH_3 on wheat plants seven days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE III



EXPLANATION OF PLATE IV

Fig. 1 The effect of NH_4NO_3-NH_3 on wheat plants 18 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of NH_4SCN-NH_3 on wheat plants 18 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE IV

Fig. 1

Fig. 2

EXPLANATION OF PLATE V

Fig. 1 The effect of NH_4I-NH_3 on wheat plants 18 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of NaI-NH_3 on wheat plants 18 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE V

Fig. 1

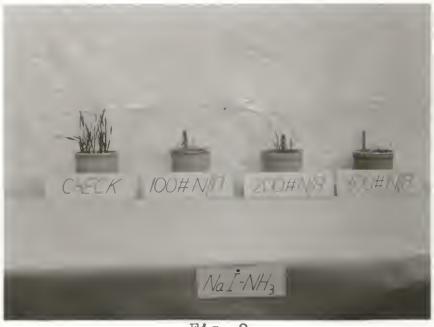


Fig. 2

EXPLANATION OF PLATE VI

Fig. 1 The effect of urea on growth of wheat when applied at the rate of 100, 200, and 300 pounds per acre.

Fig. 2 The effect of NH_4NO_3 on growth of wheat when applied at the rate of 100, 200, and 300 pounds per acre.

PLATE VI

Fig. 1

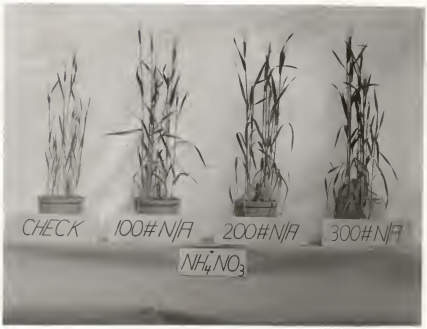


Fig. 2

EXPLANATION OF PLATE VII

Fig. 1 The effect of ureaform on growth of wheat when applied at the rate of 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of NH_4NO_3-NH_3 on growth of wheat when applied at the rate of 100, 200, and 300 pounds of nitrogen per acre.

PLATE VII

Fig. 1

Fig. 2

EXPLANATION OF PLATE VIII

Fig. 1 The effect of NH_4SCN-NH_3 on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of $NaSCN$-NH_3 on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE VIII

Fig. 1

Fig. 2

EXPLANATION OF PLATE IX

Fig. 1 The effect of NH_4Br-NH_3 on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of NH_4NO_3-NH_3 on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE IX

Fig. 1

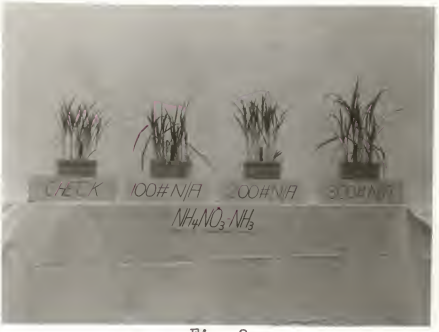


Fig. 2

EXPLANATION OF PLATE X

Fig. 1 The effect of urea on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

Fig. 2 The effect of NH_4NO_3 on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE X

Fig. 1

Fig. 2

EXPLANATION OF PLATE XI

The effect of ureaform on millet plants 171 days after application. Rates of application were 100, 200, and 300 pounds of nitrogen per acre.

PLATE XI

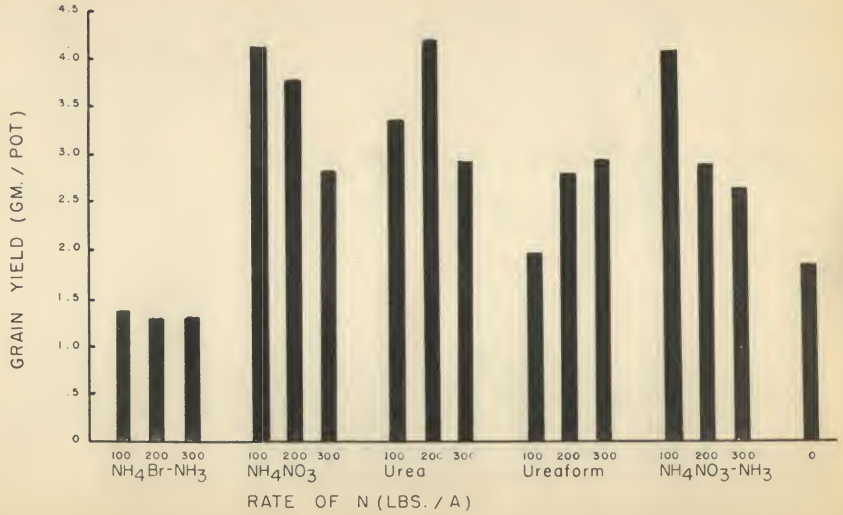


Fig. 1 Effect of various fertilizer treatments on wheat grain yield.

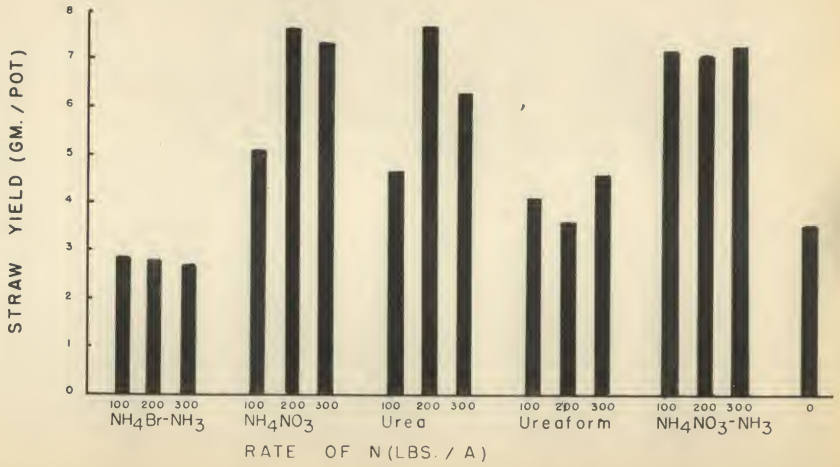


Fig. 2 Effect of various fertilizer treatments on wheat straw yield.

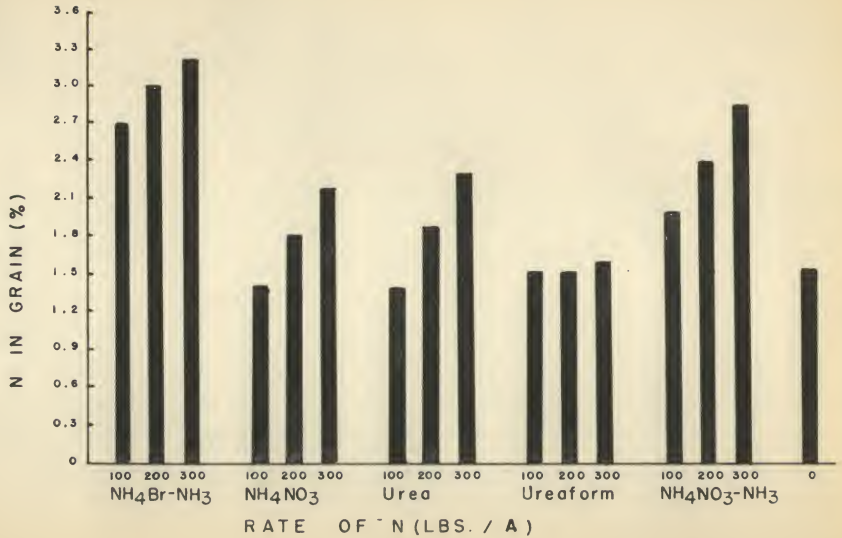


Fig. 3 Effect of various fertilizer treatments on per cent nitrogen in wheat grain.

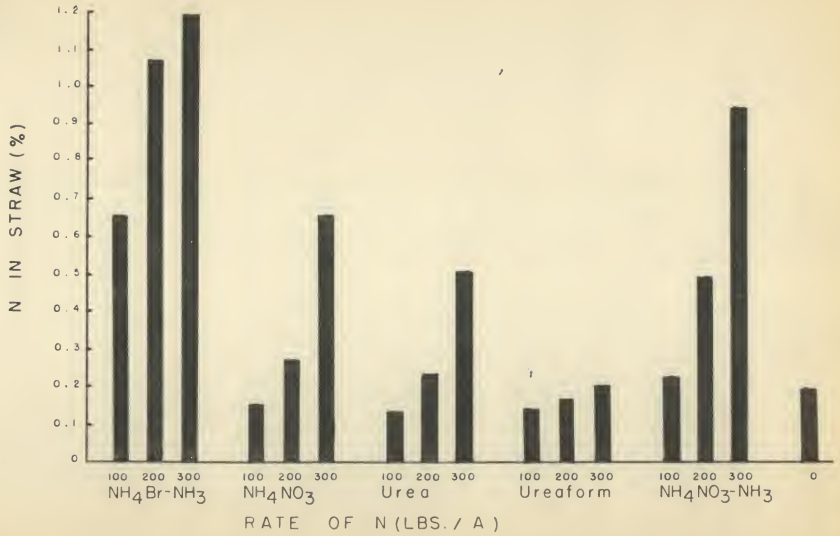


Fig. 4 Effect of various fertilizer treatments on per cent nitrogen in wheat straw.

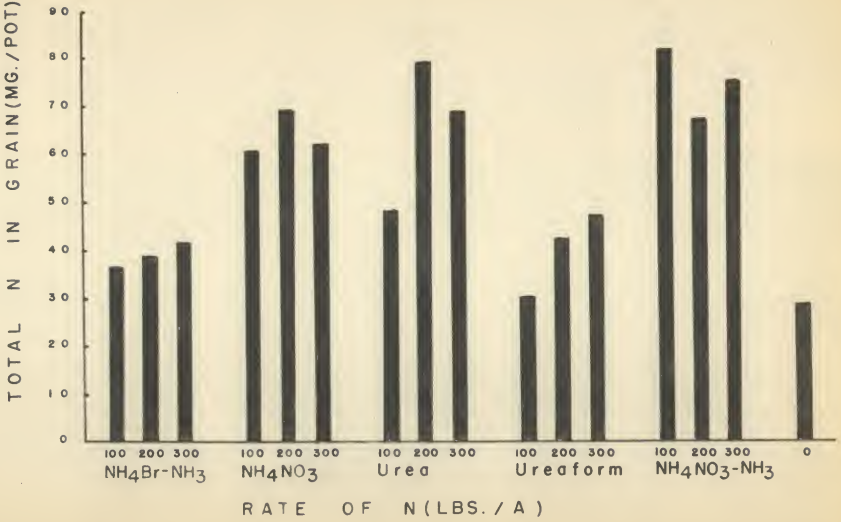


Fig. 5 Effect of various fertilizer treatments on total nitrogen in wheat grain.

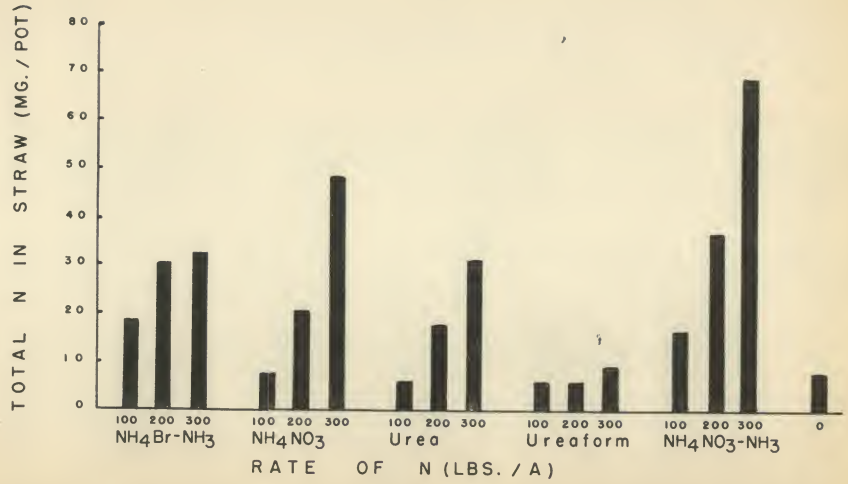


Fig. 6 Effect of various fertilizer treatments on total nitrogen in wheat straw.

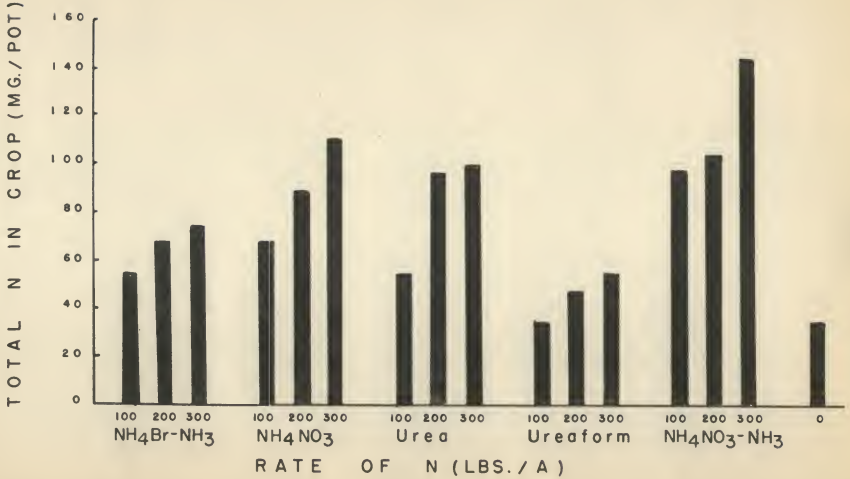


Fig. 7 Effect of various fertilizer treatments on total nitrogen in wheat.

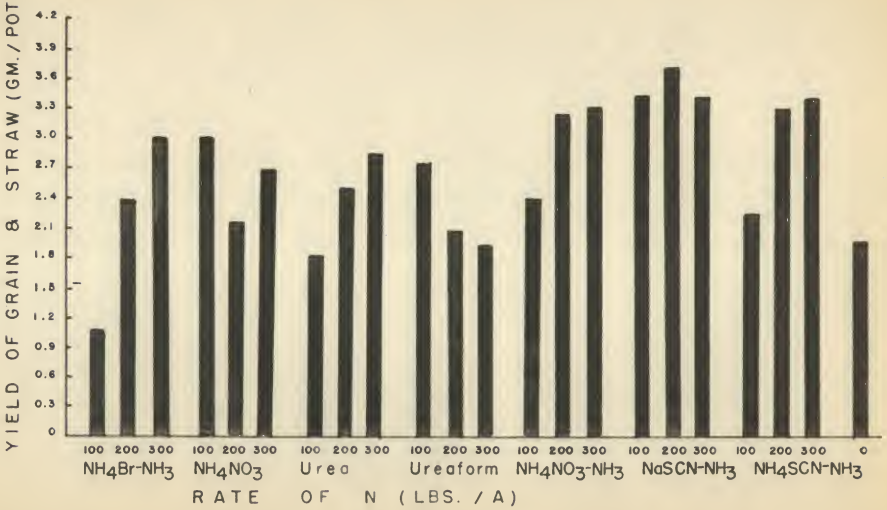


Fig. 8 Effect of various fertilizer treatments on crop yield of millet.

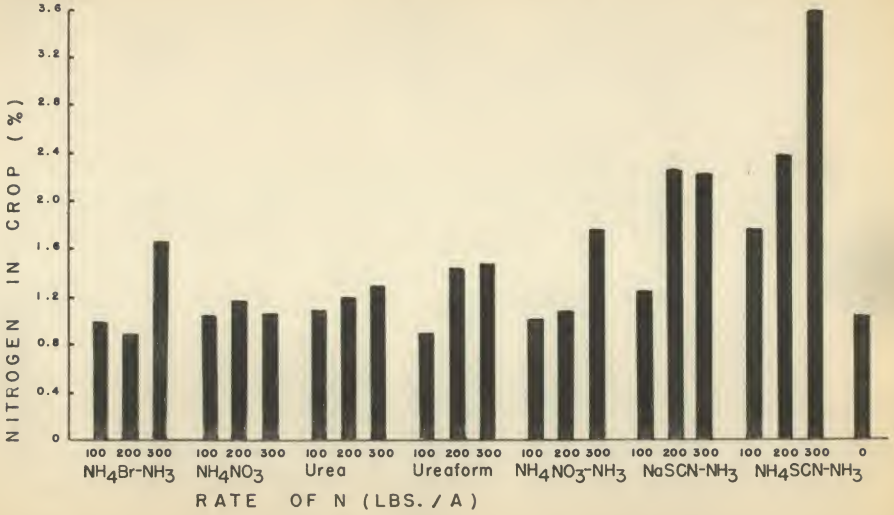


Fig. 9 Effect of various fertilizer treatments on per cent nitrogen in millet.

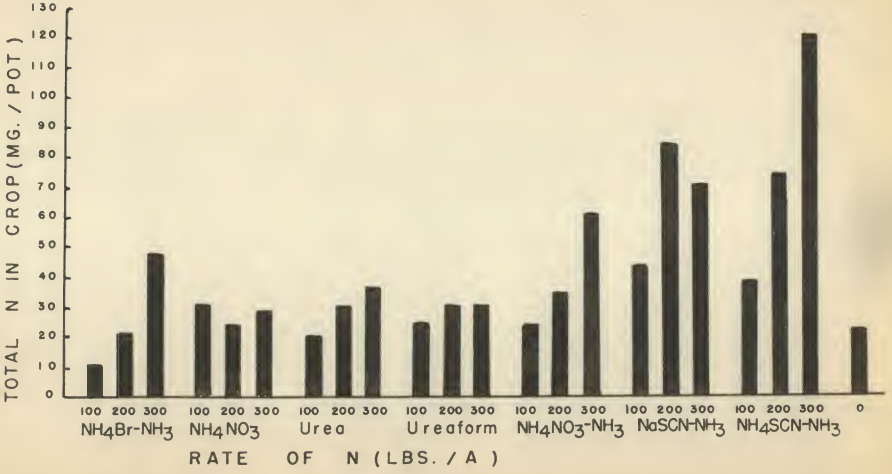


Fig. 10 Effect of various fertilizer treatments on total nitrogen in millet.

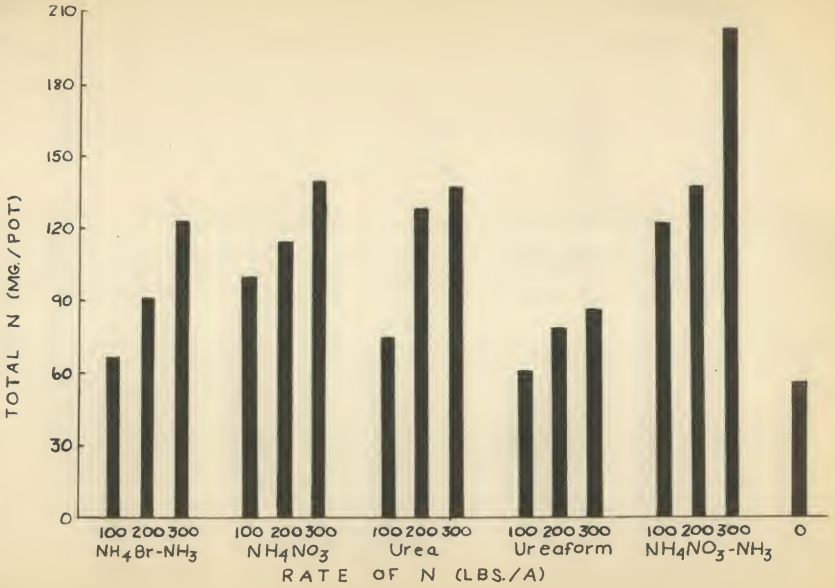


Fig. 11 Effect of various fertilizer treatments on total nitrogen uptake in combined wheat and millet crops.

A STUDY OF SEVERAL NITROGENOUS COMPOUNDS AS FERTILIZER MATERIALS

by

MARVIN FRED ZIMMERMAN

B. S., Kansas State College
of Agriculture and Applied Science, 1953

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1957

Nitrogen, because of its important role in plant growth and its loss from soil in humid areas, is applied to many soils in a variety of forms.

Nine nitrogenous compounds, of which two have been studied quite extensively, were used in this study. Ammonium nitrate and urea were included for purpose of comparison. Others used were ureaform, NH_4NO_3-NH_3, NaSCN-NH_3, NH_4SCN-NH_3, NH_4I-NH_3, NaI-NH_3 and NH_4Br-NH_3. The latter six are liquid types with NH_3 used as a solvent. Ureaform is a combination of urea and formaldehyde.

The experiment was conducted in the greenhouse with soil from the Ashland Agronomy Farm. After the soil had been thoroughly mixed a constant amount of 2,000 grams was put in each of 170 containers. Spring wheat seeds and an equivalent amount of 500 pounds per acre of triple superphosphate were applied at the same time.

After the wheat seeds had started to emerge the various fertilizers were applied at the rates of 100, 200, and 300 pounds of nitrogen per acre. The fertilizer applications were replicated six times and eight containers were used as controls. The wheat in the containers which had fertilizer applications that were not toxic was allowed to mature and was then harvested, dried, weighed and the amount of nitrogen determined.

Millet was planted in all of the containers about five months after the original application of fertilizer but no

additional nutritive elements were added at this time. When millet had matured it was harvested, dried, weighed and nitrogen content determined.

Use of $NaSCN-NH_3$, $NH_4SCN-NH_3$, NH_4I-NH_3 and $NaI-NH_3$ proved toxic to plants when first applied. Repeated wheat plantings failed on this account.

Use of NH_4Br-NH_3 caused considerable wilting in wheat when first applied but did not kill the plants. Plants survived but the amount of growth was less than where no treatment was used.

Production of dark green, luxuriant growth occurred with use of $NH_4NO_3-NH_3$. Urea and NH_4NO_3 also produced favorable growth but not as dark green in color as was produced with $NH_4NO_3-NH_3$. Yellow plant growth occurred with use of ureaform and it was superior only to NH_4Br-NH_3 in producing increased wheat plant growth.

Greatest percentage of nitrogen in wheat plants occurred from use of NH_4Br-NH_3 but the greatest total amount in plants resulted from use of $NH_4NO_3-NH_3$. Ureaform consistently produced both the lowest percentage and total amount of nitrogen in wheat.

The $NaSCN-NH_3$ and $NH_4SCN-NH_3$ cultures no longer were toxic when the millet was planted. These cultures produced a crop of millet comparable to that produced where $NH_4NO_3-NH_3$ was used. The NH_4I-NH_3 and $NaI-NH_3$ fertilizers still were toxic with millet.

With the millet crop $NaSCN-NH_3$ and $NH_4SCN-NH_3$ behaved similarly and each produced greater nitrogen uptake than the other fertilizers. This was the first crop for these two fertilizers while the other fertilizers had produced a wheat crop. Highest millet yields were obtained from use of $NH_4NO_3-NH_3$, $NaSCN-NH_3$ and $NH_4SCN-NH_3$.

Considering the combined crops of wheat and millet, $NH_4NO_3-NH_3$ was most effective of all fertilizer materials insofar as total uptake of nitrogen was concerned. Despite its inferiority with the wheat crop, NH_4Br-NH_3 was somewhat more effective than ureaform when the combination of two crops was considered. Ureaform was least effective of all fertilizer materials in total uptake of nitrogen.